

AD-A119 881

BIRMINGHAM UNIV (ENGLAND) DEPT OF SPACE RESEARCH

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ION-ION NEUTRALIZATION.(U)  
MAY 82 D SMITH, N G ADAMS

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AFOSR-77-3260

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. Report Number AFGL-TR-82-0202	2. Govt Accession No. AD-A119 881	3. Recipient's Catalog Number
4. Title (and Subtitle)  ION-ION NEUTRALIZATION		5. Type of Report & Period Covered  Final Scientific 80 Oct 01 - 82 JAN 31
		6. Performing Org. Report Number
7. Author(s)  David Smith and Nigel G. Adams		8. Contract or Grant Number  AFOSR-77-3260E
9. Performing Organization Name and Address Department of Space Research, The University of Birmingham, P O Box 363, Birmingham B15 2TT, England.		10. Program Element, Project, Task Area & Work Unit Numbers  2310/A2 2303/G1AC
11. Controlling Office Name and Address  Air Force Geophysics Laboratory/LKB  Hanscom AFB, MA 01731 Monitor/John F. Paulson		12. Report Date  31 MAY 82
		13. Number of Pages  57
14. Monitoring Agency Name and Address  European Office of Aerospace, Research and Development, London, England.		15.  Unclassified
16. & 17. Distribution Statement  Approved for public release; distribution unlimited.		
18. Supplementary Notes		
19. Key Words  Ionic Recombination, Electronic Recombination Electron Attachment, Flowing Afterglow Plasma.		
20. Abstract A variable-temperature FALP/SIFT apparatus has been built which combines the essential features of the versatile Flowing Afterglow/Langmuir Probe (FALP) and Selected Ion Flow Tube (SIFT) apparatuses. It has been used to determine the coefficients for the recombination reactions of $\text{NO}^+$ and $\text{O}^+$ ions with electrons over the temperature range 200-600 K and for the attachment reactions of $\text{SF}_6$ , $\text{CCl}_4$ and $\text{CF}_4$ with electrons at 300 K. The results of these studies are reported and are shown to resolve some of the differences which are apparent between the result of previous studies of some of these reactions. A reassessment, based on laboratory data, of the ion-ion recombination coefficients appropriate to the stratosphere is also presented and the new values are in good agreement with those derived from in-situ stratospheric observations by other workers.		

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## PREFACE

This work is part of a larger programme of ionic reaction studies at thermal energies conducted by the authors of this report. The overall programme includes studies of ion-molecule reactions, ion-ion recombination, electron-ion recombination, electron attachment and other plasma reaction processes. The work is largely intended as a contribution to the physics and chemistry of natural plasmas such as the ionosphere and the interstellar medium and of laboratory plasma media such as gas laser systems. A great deal of relevant data has been obtained principally by exploiting the versatile Selected Ion Flow Tube (SIFT) and the Flowing Afterglow/Langmuir Probe (FALP) techniques which were developed in our laboratory. Part of the overall programme is also supported by a grant from the Science and Engineering Research Council.

A major contribution to the work described in this report has been made by Dr. Erich Alge.

## I INTRODUCTION

The major thrust of the work carried out during the past few years under the terms of the grant has been the detailed study of binary ion-ion neutralization reactions involving ions of atmospheric significance. The data have been obtained by exploiting the Flowing Afterglow/Langmuir Probe (FALP) apparatus which was designed, developed and constructed in our laboratory. The flow tube in the original FALP apparatus was constructed from Pyrex glass and, whilst it has been possible to use it to determine the temperature variation of the recombination coefficients for some reactions, this is by no means a simple procedure since it involves the heating and cooling of this rather large ( $\sim 1\text{m}$  length, 10cm diameter) glass flow tube, an inherently dangerous procedure. Nevertheless, the apparatus has been extraordinarily successful and a great deal of data has been obtained. The FALP apparatus, its principle of operation, the many reactions investigated and the results obtained have been described and discussed in previous reports and in several published papers. Very recently we have written a detailed review of the ion-ion recombination work and this is included as Appendix 1 of this report. In this review paper, preliminary laboratory data are also presented relating to the variation with pressure of the rate coefficients for ionic recombination. During the last year we have made an assessment of the relevance of these data to ionic recombination rates in the stratosphere. The results of this study are briefly referred to in Sections II and III and also in more detail in Appendix 2.

The major effort during the last 16 months (the period with which this report is largely concerned) has been directed towards the design,

construction and evaluation of a new variable-temperature FALP/SIFT apparatus. The primary object of this was to provide an apparatus with which a variety of ionic and electronic reactions could be studied over a wide temperature range ( $\sim 80$  to 600 K) and therefore the flow tube was constructed from stainless-steel. This apparatus has both a mass selected ion injection system (the SIFT component), and a microwave discharge plasma source (which generates the afterglow plasma) associated with the Langmuir probe diagnostic (the FALP component). The constructional details of this FALP/SIFT apparatus will be reported in a future publication. It is a very versatile apparatus and will be exploited for several years to study a wide variety of plasma reaction process, including ion-molecule reactions, ionic recombination, electronic recombination and electron attachment.

Preliminary data obtained from the FALP/SIFT apparatus show it to be functioning beautifully. In this report, we present a brief summary of the exciting new data which we have recently obtained including the rate coefficients for two electron-ion recombination reactions, which are very important in the ionosphere, and new data on electron attachment reactions which have some relevance to the atmosphere and also to gas laser kinetics.

## II NEW RESULTS

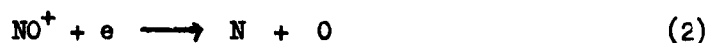
### (1) Ionic Recombination in the Stratosphere.

Laboratory data have been obtained on the pressure variation of the effective binary recombination coefficients,  $\alpha_n$ , for two reactions at low pressures (in the range 1 to 8 torr). These data, coupled with the previous data of others at higher pressures, has led us to recognize

that the increase of the ionic recombination rate with decreasing altitude in the stratosphere is more rapid than our previous estimates had indicated. We have therefore reconsidered this important problem and produced a revised profile of  $\alpha_T$  versus altitude in the stratosphere and this is given in Appendix 2. These new estimates indicate that  $\alpha_T$  is almost a factor of two larger in the altitude range 30 - 40 km than our previous estimates had indicated. These new estimates are in close accord with those deduced from in-situ measurements of steady state ion densities and ionization production rates (Rosen and Hofmann, 1981) and as such indicate that the  $\alpha_T$  versus altitude profile in the stratosphere is now well established.

(ii) Electron-Ion Dissociative Recombination

With the FALP/SIFT apparatus we are also able to measure electron-ion recombination coefficients,  $\alpha_e$ , over the available temperature range and we have initiated a major programme of such measurements. For the initial studies, we chose to investigate the temperature dependence of  $\alpha_e$  for the ionospherically important reactions :



Reaction (1) has previously been studied extensively at room temperature using a variety of techniques and  $\alpha_e$  (1) at room temperature is well established to be  $2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ . We firstly re-measured this parameter and obtained a value identical to the accepted value. The temperature dependences of these coefficients have been less well studied, although those for both reactions (1) and (2) have been determined by Biondi and his co-workers in pulsed afterglow plasmas over a limited temperature range of  $T_e = T_i = T_g$  (electron, ion and gas temperatures respectively) and over



a much wider range of  $T_e$  (for which  $T_e > T_i, T_g$ ) (Kasner and Biondi, 1968; Mehr and Biondi, 1969; Huang et al, 1975). Walls and Dunn (1974) using an ion trap experiment have also derived the temperature dependences of  $\alpha_e$  for both reactions (1) and (2) from their measurements of cross-sections as a function of electron energy. Our experiments (in which  $T_e = T_i = T_g$ ) indicate that  $\alpha_e$  (1) is given by :

$$\alpha_e (1) = 2.0 \times 10^{-7} \left[ \frac{T}{300} \right]^{-0.68} \text{ cm}^3 \text{ s}^{-1}$$

over the temperature range 200-600 K and this is in good agreement with the other studies cited above.

For reaction (2), a serious difference exists between the previous afterglow data and the trapped ion data, the former indicating a less rapid reduction of  $\alpha_e$  with increasing temperature above 400 K. We therefore thought it to be very important to investigate this reaction and our results indicate that  $\alpha_e$  (2) is given by :

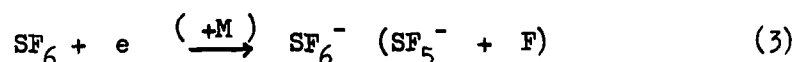
$$\alpha_e (2) = 4.2 \times 10^{-7} \left[ \frac{T}{300} \right]^{-0.91} \text{ cm}^3 \text{ s}^{-1}$$

again over the limited temperature range 200 - 600 K. Whilst we are involved in further careful checks of our data for this reaction prior to writing a detailed paper for publication, the results clearly favour the temperature variation derived from the ion-trap experiment rather than from the previous afterglow experiment, a somewhat surprising result. It is interesting to note that the  $\alpha_e$  (2) deduced from the AE satellite data also favours the ion trap data (Torr and Torr, 1978).

### (iii) Electron Attachment

This is an important type of reaction which can rapidly convert free electrons to negative ions in ionized gases containing electronegative

species. It is therefore an important process in the atmosphere and it also plays a vital role in rare gas/halide lasers (e.g. Shaw, 1979). The cross-sections for many electron attachment reactions as a function of electron energy have been obtained using a variety of techniques (see, for example, the review paper by Christophorou, 1971) but relatively few direct measurements have been made of the rate coefficients for such reactions in the thermal energy regime. The rate coefficient,  $\beta(3)$  for the very rapid reaction :

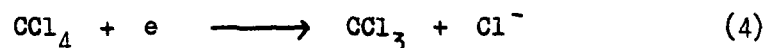


has been measured in a flowing afterglow by Fehsenfeld (1970) who obtained a temperature independent value for  $\beta(3)$  of  $2.2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ , and showed that the channel leading to the  $\text{SF}_5^-$  became increasingly favoured with increasing temperature. Later, Sides et al (1976) using a similar technique obtained a value for  $\beta(3)$  which was some 5 to 8 times smaller than that of Fehsenfeld. Our experiments indicate a  $\beta(3)$  at 300 K of  $(4.5 \pm 0.5) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ , i.e. about a factor of two greater than Fehsenfeld's value and also greater than the largest value of  $3.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  previously obtained by Mahan and Young (1966).

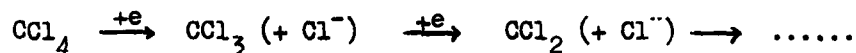
A possible source of errors in the previous measurements of these very rapid attachment coefficients is that if the initial electron number density in the ionized gas or plasma is too large then the reactant  $\text{SF}_6$  concentration (number density) will become significantly reduced as attachment of the electrons proceeds. This will lead to a slower-than-exponential reduction in the electron number density (or, equivalently an erroneously slow increase in the product negative ion number density). Under such circumstances, approximating the loss or production rates to the expected function forms will inevitably lead to erroneously small

attachment coefficients. We were readily able to demonstrate this phenomenon in our experiment and were able to ensure that the initial electron densities in our afterglow plasmas were sufficiently small to avoid this complication.

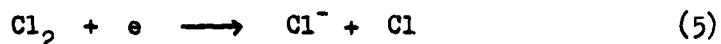
We have also studied the dissociative attachment reaction of  $\text{CCl}_4$  (Freon 14) with electrons :



This attachment is even more rapid than that for reaction (3), and the measured  $\beta$  (4) is  $(5.6 \pm 0.5) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  at 300 K. There are also indications that sequential reactions of the kind :



occur but this has not yet been substantiated. However, the quoted  $\beta$  (4) is for the first step only since it was ensured, as for the  $\text{SF}_6$  experiment, that the initial electron number density was much less than the  $\text{CCl}_4$  number density. We have also measured  $\beta$  values for several other freons and have observed that each  $\beta$  value is smaller than that for Freon 14. These data are as yet only preliminary. We have also a firm value of  $\beta$  for the reaction :



$\beta$  (5) is measured to be  $(3.7 \pm 0.5) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  which (perhaps significantly) for this much slower reaction is in close agreement with the value of  $(3.7 \pm 1.8) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  obtained by Sides et al (1976).

### III SUMMARY AND CONCLUSIONS

The new variable temperature FALP/SIFT apparatus is fully operational and new, interesting data are now being obtained. A start

has been made on what we anticipate will be major programmes of study of electron-ion recombination and electron attachment reactions of interest in natural plasmas, especially in the atmosphere, and in gas lasers. The preliminary data alluded to in this report illustrate the versatility of the technique in the study of a wide range of plasma reaction processes.

A summary of the new work discussed briefly in Section II is as follows.

- (a) The coefficients for ion-ion recombination, in the mesosphere and the stratosphere are now defined to better than  $\pm 50\%$ , whereas more laboratory work is required to establish the values appropriate to the higher pressure troposphere. Deionization rates in the troposphere may be strongly influenced by the presence of aerosols and this has to be recognized when considering deionization rates (Rosen and Hofmann, 1981).
- (b) The temperature dependences of the coefficients for electronic recombination of the ionospherically important ions  $O_2^+$  and  $NO^+$  in their ground vibronic states with electrons have been clearly defined over the temperature range 200 - 600 K.
- (c) The coefficients for electron attachment to  $SF_6$  and for the dissociative attachment reactions of electrons with  $CCl_4$  and  $Cl_2$  have been measured. The coefficient obtained for the  $SF_6$  reaction is significantly greater than those previously obtained and this may be an important consideration in atmospheric release experiments. The dissociative attachment with  $CCl_4$  is also very fast and therefore  $CCl_4$  might be a more appropriate choice for such experiments.

Detailed papers on the results of the studies briefly described in (ii) and (iii) of Section II will be written in the near future.

During the coming year, more detailed studies of ion-ion recombination electron-ion recombination, electron attachment and positive and negative ion molecule reactions will be carried out using the new FALP/SIFT apparatus. It promises to be a very productive period.

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APPENDIX 1

STUDIES OF ION-ION RECOMBINATION  
USING FLOWING AFTERGLOW PLASMAS.

To be published in the proceedings of the NATO  
Advanced Study Institute on Ion-Ion and Electron-  
Ion Collisions. Eds. F. Brouillard and J. Wm. McGowan  
Plenum Press, 1982.

## STUDIES OF ION-ION RECOMBINATION USING FLOWING AFTERGLOW PLASMAS

David Smith and Nigel G. Adams

Department of Space Research  
University of Birmingham,  
Birmingham B15 2TT, England.

### 1. INTRODUCTION

Binary positive-ion negative-ion mutual neutralization viz:



can be an important loss process for ionization in low pressure ionized gases containing electron attaching species, for example oxygen, oxides of nitrogen, halogens, etc. It is therefore potentially important in many familiar plasma media such as flames, gas lasers and the Earth's ionosphere. Because of the Coulombic nature of these interactions the cross-sections,  $\sigma_i$ , for the process at low energies can be very large ( $\approx 10^{-12} \text{ cm}^2$ ) but as we shall see  $\sigma_i$  varies over a few orders of magnitude depending on the nature of the ionic species involved in the reactions and on the interaction energy. At the onset it should be stated that in this paper for the sake of simplicity we use the term binary ionic recombination to describe the process although this is clearly a misleading description.

At gas pressures which are sufficiently high such that three-body collisions occur, the process of ternary ionic recombination viz:



occurs and becomes increasingly dominant over the binary process as the gas pressure (or gas number density,  $M$ ) increases. In the Earth's atmosphere, both the binary and ternary processes occur; between the altitudes 30-60 kms (in the lower mesosphere and upper stratosphere) the binary process dominates and below 30 kms (in the lower

stratosphere and the troposphere) the ternary process dominates. It was to fulfil the need for data for atmospheric deionization rate calculations that the ionic recombination work in our laboratory (which is summarised in this paper) was initiated. The relevance of our data to atmospheric research will be referred to from time-to-time. To date only the binary process has been studied in detail in our laboratories, largely due to the limitations of the present flowing afterglow technique used, but some preliminary data have been obtained on the ternary process and these are briefly referred to at the end of this paper.

The major objective of the paper is to describe the advances that have been made in the study of thermal energy ionic recombination using the flowing afterglow/Langmuir probe (FALP) technique which has been developed and exploited during the last few years to study ionic recombination and other low temperature plasma processes. However, to set this work in context, it is pertinent first to briefly refer to the important contributions to ionic recombination studies which were made prior to the FALP work.

The earliest studies of ionic recombination were made in weakly ionized gases at high pressures ( $\sim 1$  atmosphere) and as such were concerned with the ternary process (2) (Mächler, 1936; Sayers, 1938). No mass identifications of the ions involved in the reactions were made although it seems clear now that both the positive and negative ions were probably "cluster ions", that is consisting of a strongly bonded core ion (e.g.  $\text{H}_3\text{O}^+$ ,  $\text{NO}_3^-$ , etc.) to which molecules (usually polar molecules such as  $\text{H}_2\text{O}$ ) are bonded via weaker polarization forces. These cluster ions are expected to be the dominant species in ionized gases containing polar molecules and are known to be the dominant species in the lower atmosphere. We shall be concerned with the binary reactions of cluster ions such as  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  and  $\text{NO}_3^-(\text{HNO}_3)_m$  in a later section of this paper. Reviews of the early work have been given by Sayers (1962) and by Flannery (1976), the latter including the development of the theoretical aspects of the subject.

Experiments carried out in collision-dominated media are concerned with the measurement of rate coefficients rather than cross-sections (these were measured in later beam experiments). Thus by observing the rate of loss of the ionization in the media the binary ionic recombination coefficient,  $\alpha_2$ , or the ternary ionic recombination coefficient,  $\alpha_3$ , can be obtained, since for process (1):

$$\frac{dn_{+,-}}{dt} = -\alpha_2 n_+ n_- \quad (3)$$

$$\text{and for process (2): } \frac{dn_{+,-}}{dt} = -\alpha_3 n_+ n_- [M] \quad (4)$$



where  $n_+$  and  $n_-$  are the number densities of the positive and negative ions  $[A^+]$  and  $[B^-]$  respectively and  $[M]$  is the number density of the "inert" third body support gas. Additionally in these experiments it is assumed that charge neutrality exists in the medium, i.e.  $n_+ = n_-$ . An 'effective binary coefficient' can be determined for process (2) as  $\alpha_3 [M]$ , and the earlier experiments established that the magnitude of this varied with pressure. At about 0.1 atmosphere it was  $\sim 1 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  passing through a maximum value of  $\sim 3 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  at about 1 atmosphere and then decreasing with further increase in pressure. In later similar but more sophisticated experiments by Mahan and Person (1964), studies were again made over a wide pressure range (10 - 700 Torr) but extended towards lower pressures and values of  $\alpha_2$  were obtained by extrapolation of the  $\alpha_3 [M]$  data to the limit of zero pressure. Values for  $\alpha_2$  of typically  $2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  were obtained in several different media but as before no mass analysis was carried out to determine the nature of the reactant ions. However, as Mahan (1971) recognized in his excellent review of ionic recombination, it is probable that the ions were cluster ions in several cases. This emphasised the necessity for mass identification in these and indeed all recombination experiments, and such was incorporated in the later experiments by Mahan and co-workers (Fisk et al, 1967), and also in pulsed afterglow plasma experiments (Eisner and Hirsh, 1971; Hirsh and Eisner, 1972).

With the development of the merged beam technique for ionic recombination studies (Aberth et al, 1968; Aberth and Peterson, 1970) a determined effort was made to study reactions involving various combinations of atomic and molecular positive and negative ions. Cross-sections were determined as a function of the centre-of-mass energy of two ion beams (with high laboratory energies), and in order to obtain thermal energy rate coefficients the cross-section data were extrapolated to lower energies and then averaged over a Maxwellian velocity distribution. A summary of the data obtained using this technique is given in the review by Moseley et al (1975) in which comparisons are made with theoretical calculations of the cross-sections and rate coefficients for particular reactions. Good agreement was obtained between theory and experiment for reactions involving only atomic ions whereas discrepancies were apparent for reactions involving molecular ions, the experimental values being consistently larger than the theoretical predictions. Some of the results of the merged beam and pulsed afterglow experiments will be discussed further in relation to the FALP data.

The basic ideas in the theoretical description of binary ionic recombination are also included in the review by Moseley et al (1975). These ideas are based on the premise that electron transfer occurs at avoided crossings of the reactant ionic and product covalent potential curves for the system, and Landau-Zener theory is used to calculate the cross-sections. Varying degrees of sophistication are possible depending on the nature of the reactant ions and the number

of possible product neutral states. For the simplest systems, that is for some atomic systems in which the number of product states is few then detailed close coupling calculations are possible (Olson 1977). However, for molecular systems in which a large number of product states are possible then this rigorous procedure is not practicable and a less rigorous procedure has been developed (Olson, 1972) - the so-called absorbing sphere model. This approach avoids the protracted procedure of calculating transition probabilities for all curve crossings and instead defines an 'absorbing sphere' inside which reaction occurs with unit probability. The predictions of this model will be related to the FALP data below. The theory relating to the ternary process is summarised in the reviews by Mahan (1973) and Flannery (1976).

## 2. THE FLOWING AFTERGLOW/LANGMUIR PROBE (FALP) TECHNIQUE

The thermalised afterglow plasma is a medium in which a wide range of ionic processes can be investigated under well defined conditions. The time-resolved or pulsed (stationary) afterglow was first exploited by S.C. Brown and co-workers using microwave cavity and mass spectrometric diagnostics and this technique has since been exploited to great effect by M.A. Biondi and co-workers to study electron-ion dissociative recombination. Pulsed afterglows have also been used by H.J. Oskam and co-workers, D. Smith and co-workers and by W.C. Lineberger and co-workers to study a variety of plasma processes. Brief summaries of this early work are given in the books by McDaniel (1964) and by McDaniel and Mason (1973).

The flowing afterglow technique was first developed and exploited by Ferguson, Fehsenfeld and Schmeltekopf (1969) to study ion-molecule reactions at thermal energies. This technique and other flow tube techniques have been discussed in a recent review (Smith and Adams, 1979a). In essence, a flowing afterglow consists of a flow tube along which a carrier gas is constrained to flow by the action of a large Roots-type pump, and in which ionization is created in the upstream region by a gas discharge or some other type of ion source. An afterglow plasma is thus distributed along the flow tube and under favourable conditions the charged particle energies will be relaxed in the afterglow to those appropriate to the carrier gas temperature. Distance along the flow tube and afterglow time are coupled via the flow velocity of the plasma which can readily be determined (see Section 2.2). The flowing afterglow has the precious advantage over the stationary afterglow that reactant gases can be introduced into the thermalized plasma and thus are never exposed to the high-energy electrons in the upstream discharge/ion source. Thus unwanted molecular excitation and dissociation can be avoided and greater control can be exercised in the creation of suitable plasma media.

A standard diagnostic technique used in most flowing afterglow experiments is quantitative mass spectrometry which is achieved by positioning a differentially pumped mass spectrometer at the downstream end of the flow tube. This is the only diagnostic required in the determination of ion-molecule reaction rate coefficients but for the determination of the rate coefficients for ionic and electronic recombination, absolute charged particle number densities are required and it is for this purpose that we developed the Langmuir probe technique (described in Section 2.2) for use in afterglow plasmas. The successful application of the FALP technique to the study of ionic recombination is the culmination of several years of development and exploitation of the probe technique first in stationary afterglows and then in flowing afterglows. This work has led to an understanding of afterglow plasma processes which has proved invaluable in our efforts to create appropriate plasma conditions for ionic recombination studies and in the interpretation of FALP data. These aspects of the work will now be discussed briefly.

## 2.1 The Flowing Afterglow Plasma

In the FALP experiments, the carrier gas most often used is pure helium at about 1 torr pressure, and a microwave cavity discharge is created in it to establish a sufficiently high ionization density in the afterglow to permit the study of recombination loss processes above other loss processes. In these experiments, small quantities of reactant gases can be added either upstream of the discharge or downstream into the afterglow (see Fig.1). Often two different reactant gases are used simultaneously, one being introduced upstream and one downstream. For the ionic recombination studies one of the gases is invariably an electron attaching gas from which negative ions are created. Other processes which can occur in these plasmas are discussed below and it is an appreciation of their relative rôles which allows the creation of suitable plasma media to study the various individual processes. A major objective is to establish afterglow plasmas in which the loss of the particular charged particle species occurs almost solely by the process which it is desired to study.

**2.1.1 Ambipolar diffusion.** This is always a finite loss process for ions and electrons in bounded plasmas. It has been studied for its own sake (e.g. see McDaniel and Mason, 1973) and we have studied it in both stationary afterglows (e.g. Smith and Cromey, 1968; Smith and Copsey, 1968; Smith et al, 1972a), and in the FALP apparatus (Smith et al, 1975) by observing the electron density gradient along a pure helium electron-ion afterglow plasma. The time decay of the electron density,  $n_e$ , and the positive ion density,  $n_+$ , is described by:

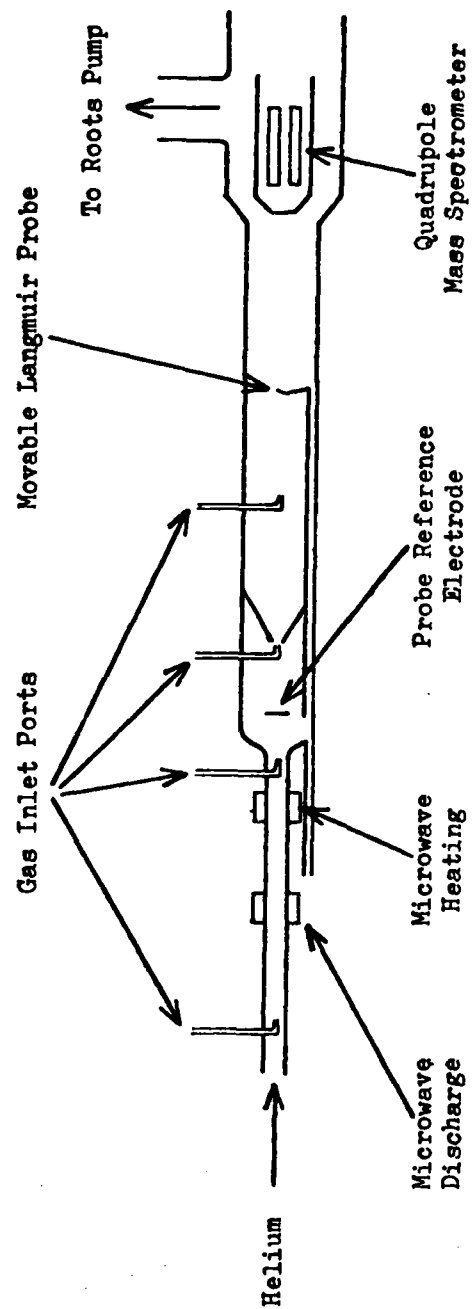


Fig.1 Schematic diagram of the Flowing Afterglow/Langmuir Probe (FALP) apparatus.

$$\frac{dn_{+,e}}{dt} = D_a \nabla^2 n_{+,e} \quad (5)$$

The solution of equation (5) is well understood for the cylindrical geometry of the flowing afterglow (Bolden et al, 1970; Adams et al, 1975) and thus the ambipolar diffusion coefficient,  $D_a$ , can be determined.  $D_a$  is inversely proportional to the pressure,  $p$ , ( $D_a \sim 1/p$ ) and so in order to study other charged particle loss processes, ambipolar diffusion is inhibited by operating at a suitably high pressure. Additionally  $D_a$  is directly dependent on the electron temperature and thus low electron temperatures diminish ambipolar diffusion losses.

**2.1.2 Electron temperature relaxation.** The 'hot' electrons which exist in the microwave discharge are cooled in collisions with positive ions and carrier and reactant gas atoms or molecules during their passage down the flow tube. It is important to be able to estimate the rate of cooling of the electrons so that the position in the afterglow at which they are thermalized can be determined. Under favourable conditions, the Langmuir probe can be used to measure the electron temperature (Dean et al, 1972; Smith, 1972) and this has been achieved in both stationary and flowing afterglows (Smith et al, 1972a; Dean et al, 1974). The rate of electron temperature relaxation is described by:

$$\frac{dT_e}{dt} = -\frac{1}{\tau} (T_e - T_{+,n}) \quad (6)$$

$T_e$ ,  $T_+$  and  $T_n$  are the temperatures of the electron gas, positive ion gas and carrier gas respectively and  $T_+ \approx T_n$  in these plasmas. The time-constant  $\tau$  describes the net effect due to electron-ion (time-constant  $\tau_{ei}$ ) and electron-neutral (time-constant  $\tau_{en}$ ) collisions such that  $\tau^{-1} = \tau_{ei}^{-1} + \tau_{en}^{-1}$ . The small fractional ionization density in these afterglow plasmas ( $\sim 10^{-6}$ ) ensures that electron-neutral collisions are the most effective. This is especially so when the neutral gas is molecular since then  $\tau_{en}$  is very short (Smith and Dean, 1975; Dean and Smith, 1975). It should be noted that  $T_e$  relaxation will be inhibited in afterglows in which metastable excited species are present due to superelastic collisions of electrons with these species. These are particularly effective in pure helium afterglows in which an electron colliding with a helium metastable can gain about 20 eV of energy. Such, however, is usually unimportant when other gases are present since Penning reactions rapidly destroy the metastable atoms.

**2.1.3 Electron attachment.** Three different processes can be distinguished, two binary and one ternary (see e.g. Massey, 1976, 1979). Thermal dissociative attachment, e.g.:

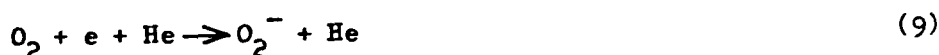


can occur rapidly when the electron affinity  $E_a$  of the electron acceptor (Cl) exceeds the dissociation energy  $E_d$  of the molecule. Non-thermal dissociative attachment, e.g.



can occur only for electron energies in excess of  $(E_d - E_a)$ , which for reaction (8) is 3.65 eV, and so this cannot occur in a thermalised afterglow. However, it can occur when oxygen is passed through the gas discharge which generates the afterglow.

The ternary attachment process, e.g.



is obviously promoted by high pressures of the catalysing third body (in this case He). The rate of loss of electrons via these processes and hence the rate of formation of negative ions is described by the relation:

$$\frac{dn_e}{dt} = -\beta_2 n_e n_n \text{ or } -\beta_3 n_e n_n [M] \quad (10)$$

for the binary and ternary processes respectively. The attachment coefficient  $\beta_2$  and  $\beta_3$  have been measured for a large number of reactions (Christophorou, 1971) and are valuable in estimating the concentrations of attaching gases needed to generate negative ions in plasma.

2.1.4 Electronic and ionic recombination. Dissociative electronic recombination e.g.



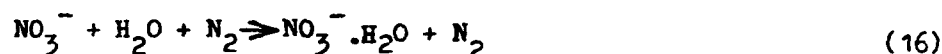
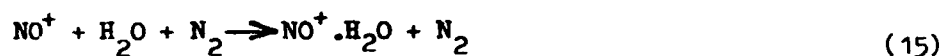
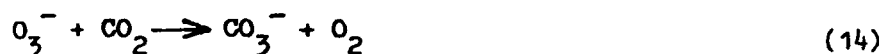
is the only effective electronic recombination process in laboratory thermalised afterglow plasmas. It is especially rapid when cluster ions are involved (Biondi, 1973; Leu et al, 1973; Bates, 1979) and can rapidly remove ionization from the plasma. The recombination coefficient,  $\alpha_e$ , is defined by:

$$\frac{dn_{e,+}}{dt} = -\alpha_e n_e n_+ \quad (12)$$

and is analogous to the ionic recombination coefficient  $\alpha_2$  defined by equation (3). Electrons and negative ions often co-exist in plasmas and so electronic and ionic recombination will be

occurring simultaneously. However  $\alpha$  is invariably much greater than  $\alpha_2$ . Ionic recombination will be discussed in detail later.

**2.1.5 Ion-molecule reactions.** Positive ions and negative ions usually react rapidly with neutral molecules at thermal energies generating new ionic species and such reactions are exploited in the ionic recombination studies described in this paper to generate appropriate ionic species in the plasmas. Ion-molecule reactions can result from either binary or ternary collisions, e.g.:



Reactions (15) and (16) are examples of association or clustering reactions and these and many other reactions are important in the Earth's atmosphere, interstellar clouds and many other plasma media (see e.g. Ferguson et al, 1979; Smith and Adams, 1980a; Dalgarno and Black, 1976; Smith and Adams, 1979b). A very large literature exists relating to reaction types, rate coefficients etc. (see for example the data compilation by Albritton, 1978) and a knowledge of this is essential when considering how to generate afterglow plasmas containing specific positive and negative ion types for recombination studies. The loss rate of a given ionic species due to, for example, ternary ion molecule reactions is described by

$$\frac{dn_{+,-}}{dt} = -kn_{+,-} n_g [M] \quad (17)$$

where  $k$  is the rate coefficient,  $n_g$  is the reactant gas concentration and  $[M]$ , as before, is the concentration of the third body.

**2.1.6 The creation of ion-ion afterglow plasmas.** In order to determine ionic recombination coefficients in plasmas it is very desirable to ensure that no plasma electrons are present since dissociative electronic recombination seriously influences the loss of ionization and confuses the interpretation of the probe data. These complications are eliminated by ensuring that sufficient electronegative gas is present in the plasma medium to promote rapid electron attachment. In the FALP experiments this is achieved by introducing a suitable concentration of the electronegative gas (e.g.  $NO_2$ ,  $Cl_2$ ,  $SF_6$ ) either upstream or downstream of the gas

discharge when negative ions are formed as described in Section 2.1.3. Additionally, as the afterglow plasma passes down the flow tube, loss of electrons occurs from the plasma via ambipolar diffusion whereas the negative ions remain trapped in the plasma by the ambipolar space charge field. Eventually at some position down the flow tube the electron density decreases to a value such that the electron Debye length in the plasma is comparable to the flow tube radius. The ambipolar field then collapses and the remaining electrons freely diffuse to the flow tube walls. Thus a positive ion/negative ion plasma remains which is devoid of electrons. We have discussed this phenomenon in detail previously in relation to both stationary and flowing afterglow plasmas (Smith et al, 1974; Smith and Church, 1976). The essential requirement in the FALP measurements of ionic recombination coefficients is to generate ion-ion plasmas consisting of appropriate ion types in sufficient densities such that loss by ionic recombination dominates diffusive loss. Clearly knowledge of the ionic reactions which generate the desired ions is required. In this respect careful use of the mass spectrometer (see Fig. 1) is essential to monitor the complex ion chemistry which occurs and to establish the nature of both the positive and the negative ions. Also both a sufficiently low carrier gas pressure and the addition of sufficient electro-negative gas are required so that a rapid transition to an ion-ion plasma occurs, yet at a carrier gas pressure sufficiently high that ionic recombination loss dominates over diffusive loss. Sometimes these requirements are counteractive and a compromise has to be adopted such as accepting the presence of more than one species of positive and/or negative ion and tolerating a reduced range of  $n_+$  and  $n_-$  values from which to obtain  $\alpha_2$  (see Section 3.1).

## 2.2 The Langmuir Probe Diagnostic

Since their inception Langmuir (electrostatic) probes have been used to great effect in the study of steady state discharges (Mott-Smith and Langmuir, 1926). The theory and practice of their operation is discussed in the book by Swift and Schwar (1970). Prior to our work however, probes had not been used satisfactorily to study decaying (afterglow) plasmas which are easily disturbed by the presence of a current-collecting electrode. In essence, the Langmuir probe is simply a small regular-shaped electrode immersed in a plasma, the potential of the probe being swept positively or negatively relative to the plasma (or space) potential. In practice, plasma potential is referenced to another electrode (see Fig. 1) of surface area much greater than that of the probe. Thus from the electron current ( $i_e$ ) vs voltage ( $V_p$ ) characteristics of an appropriately shaped probe immersed in an electron/positive-ion plasma the electron temperature,  $T_e$ , and the electron density,  $n_e$ , can be determined. Conventionally,  $n_e$  is determined from  $i_e$  at plasma potential. However plasma potential cannot be



unambiguously determined accurately (Goodall and Smith, 1968) and so we have adopted the so-called orbital-limited-current mode of current collection which has the advantage that, for a cylindrical probe, the  $n_e$  values are determined from the linear slopes of  $i_e^2$  vs  $V_p$  curves and not from a point on the  $i_e$  vs  $V_p$  curve. Thus in the electron-collecting orbital-limited-current regime;

$$i_e^2 = \frac{2A^2 n_e^2 e^2}{\pi^2 m_e} (eV_p + kT_e) \quad (18)$$

and so  $n_e$  can be determined if the probe area,  $A$ , is known. A similar expression (Smith and Plumb, 1972) can be used to deduce the positive ion density from the ion current to the probe when it is negatively biased with respect to plasma potential, although in this case the probe current is much smaller. This asymmetry in the  $i$  vs  $V$  characteristic is due to the smaller mobility of positive ions relative to electrons. The successful application of this probe technique to stationary and flowing afterglow plasmas results largely from the recognition that very small probes must be used in these decaying plasmas in order to avoid disturbing the plasma by drawing excessive current. A typical cylindrical probe used in our afterglow work is a short tungsten wire of length 0.5 cm and diameter  $2.5 \times 10^{-3}$  cm. These probes have been used successfully to study a variety of afterglow plasma problems and the results have been reported in the literature. For example, the probes have been used to study the phenomenon of diffusion cooling of electrons and have measured electron temperatures as low as 90 K (Smith et al, 1972a), to determine  $\alpha_e$  for reaction (11) which is in excellent agreement with the  $\alpha_e$  obtained using microwave diagnostics (Smith and Goodall, 1968; Plumb et al, 1972), and to follow the transition from electron-ion to ion-ion afterglow plasma (as discussed in Section 2.1.6) by monitoring the ambipolar fields within afterglow plasmas (Smith et al, 1974). A detailed appraisal of the application of the technique to the study of electron/ion afterglow plasmas has also been reported (Smith and Plumb, 1972).

This probe technique has also been adopted for use in ion-ion afterglow plasmas. In such plasmas, equation (18) is modified to:

$$i_{+,-}^2 = \frac{2A^2 n_{+,-}^2 e^2}{\pi^2 m_{+,-}} (eV_p + kT_{+,-}) \quad (19)$$

Here the electron mass,  $m_e$ , has been replaced by the positive ion or negative ion mass,  $m_+$  or  $m_-$  and to determine  $n_+$  and/or  $n_-$  then obviously  $m_+$  and/or  $m_-$  must be known. In practice, the probe is swept both positively and negatively relative to plasma potential

and so both negative and positive ion currents are collected in accordance with equation (19). The slopes of the  $i^2$  vs  $V_p$  and the  $i^2$  vs  $V_p$  provide a value for the mass ratio  $m^+/m^-$  of the ions in the plasma. When more than one species of positive or negative ion is present then a mean ionic mass ratio is obtained (Smith et al, 1978) and this can be a useful indicator of the ion content of the flowing afterglows in positions upstream of the mass spectrometer sampling position (Fig. 1).

All of the data obtained to date using the FALP technique have been acquired using a glass flow tube about 100 cm long and 10 cm diameter. The Langmuir probe can be located anywhere along the flow tube axis from a position some 10 cm downstream of the microwave discharge to about 10 cm upstream of the mass spectrometer sampling orifice, a movement of about 70 cms. Thus the axial ion and/or electron density gradients can be determined over this appreciable length,  $z$ , of the afterglow column. To relate  $z$  to afterglow time in order to determine  $\alpha_2$ , the plasma flow velocity,  $v_p$ , is measured by pulse-modulating the microwave discharge and monitoring the passage of the plasma density disturbance along the flow tube using the probe.  $v_p$  is typically  $10^4$  cm s<sup>-1</sup>. An experimental and theoretical appraisal of the dynamics of these afterglow plasmas has been carried out and this has been reported in detail in the literature (Adams et al, 1975). Further reference to the essential details of the FALP technique will be given as appropriate in the following sections.

### 3. DETERMINATION OF BINARY IONIC RECOMBINATION COEFFICIENTS: SIMPLE MOLECULAR IONS

We define here "simple" molecular ions as those which are organised by normal covalent bonds (e.g.  $\text{NO}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{SF}_6^-$ ) in contrast to "cluster" ions (e.g.  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ,  $\text{NO}_3^-(\text{HNO}_3)_m$ ). The reactions of cluster ions are considered later.

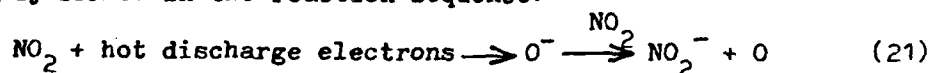
#### 3.1 Room Temperature Measurements

Several reactions involving molecular ions have been studied using the FALP but none more thoroughly than the reaction:



We will therefore briefly discuss the experimental details which were involved in the study of reaction (20) to exemplify the experimental approach (discussed in detail by Smith and Church, 1976). Pure helium was used as the carrier gas at a pressure,  $p_0$ , of typically 0.6 Torr, although  $p_0$  was varied over a limited

range (0.4 to 1.0 Torr) to check for any three-body contribution to the ionic recombination loss. Nitrogen dioxide,  $\text{NO}_2$ , at a partial pressure  $\sim 1$  mTorr, was added to the carrier gas upstream of the microwave discharge, this being a sufficient concentration to establish an ion-ion plasma some 20 cm downstream of the discharge. The mass spectrometer indicated that  $\text{NO}^+$  and  $\text{NO}_2^-$  were essentially the only ion species present in the downstream afterglow region. The  $\text{NO}^+$  was formed via direct electron collisional ionization of  $\text{NO}_2$ , and via the  $\text{He}^+ + \text{NO}_2$  and  $\text{He}^m + \text{NO}_2$  reactions. The  $\text{NO}_2^-$  was largely formed in the reaction sequence:



The Langmuir probe was used to measure both  $n_+$  and  $n_-$  along the ion-ion afterglow plasma column and also the plasma flow velocity,  $v_p$ . Ambipolar diffusion and binary ionic recombination are the competing loss processes for ions in the plasma. Therefore:

$$v_p \frac{dn_{+,-}}{dz} = \frac{dn_{+,-}}{dt} = D_{+,-} \nabla^2 n_{+,-} - \alpha_2 n_{+,-}^2 \quad (22)$$

At low pressures and low  $n_+$ ,  $n_-$  the diffusive term dominates the loss of ionization whereas at higher pressures and higher  $n_+$ ,  $n_-$  then the recombination term dominates as is required for these studies. The requirement is that  $D_{+,-} / \Lambda^2 \ll \alpha_2 n_{+,-}$  (where  $\Lambda$  is the characteristic diffusion length, Adams et al, 1975) and if  $D_{+,-}$  and  $\alpha_2$  can be estimated then the pressure and ionization density required to ensure that ionic recombination is the dominant process may be estimated. For a recombination controlled plasma:

$$\left( \frac{1}{n_{+,-}} \right)_t - \left( \frac{1}{n_{+,-}} \right)_0 = \alpha_2 t \quad (23)$$

and a plot of reciprocal density versus time will be linear and  $\alpha_2$  can be obtained from the slope. Example plots are given in Fig. 2. Note that for the  $\text{NO}^+ + \text{NO}_2^-$  reaction the initial ionization density ( $n_{+,-}$ ) is about  $3 \times 10^{10} \text{ cm}^{-3}$ , which is typical of FALP experiments, and that for large  $z$  (late afterglow times) then characteristic upcurving of the plots occurs due to the increasing importance of diffusive loss at the lower ionization densities. For the  $\text{SF}_3^+ + \text{SF}_5^-$  reaction, ( $n_{+,-}$ )<sub>0</sub> is significantly larger this being a manifestation of the more rapid electron attachment in plasmas containing  $\text{SF}_6$ . Note also the close equivalence of the derived  $n_+$  and  $n_-$  indicating the consistency of the probe technique in the positive ion and negative ion collecting modes and that the correct ionic masses were used to calculate  $n_+$  and  $n_-$ . Since the probe data provides a value of the mass ratio,  $m_+/m_-$ , then in circumstances where the mass of only one ionic species can be ascertained then that of the other can be deduced. This approach

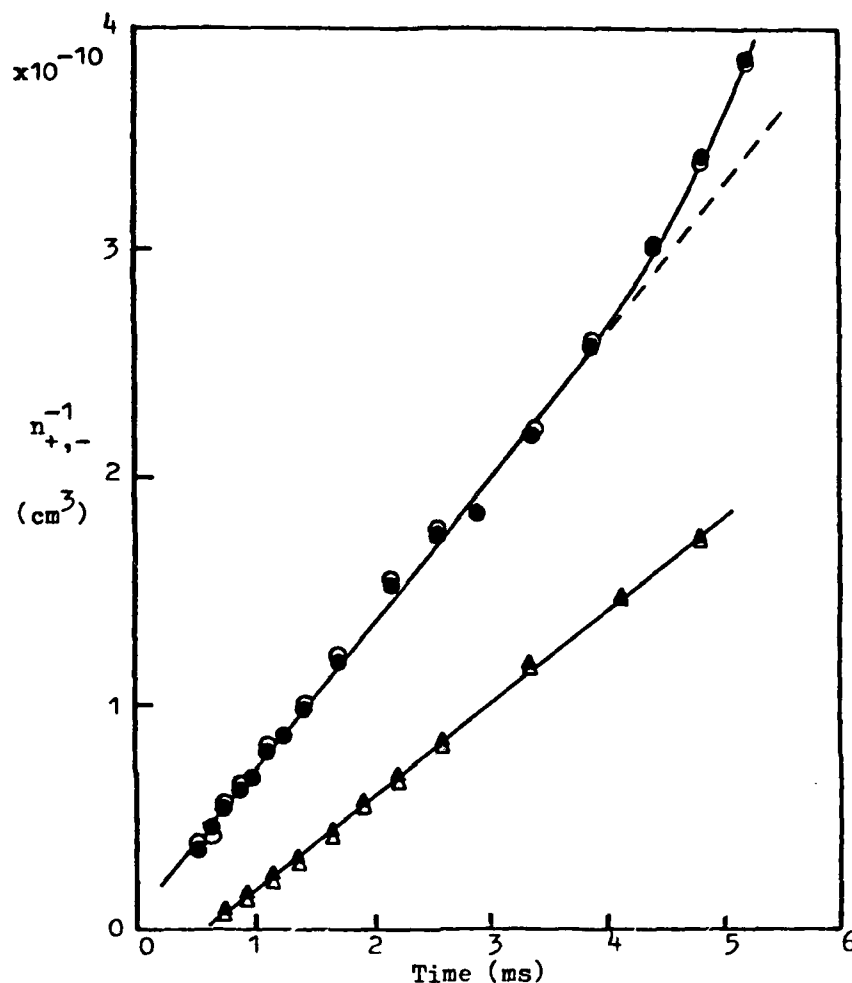


Fig.2 Reciprocal positive ion densities (filled symbols) and reciprocal negative ion densities (open symbols) as a function of afterglow time for the reaction  $\text{NO}^+ + \text{NO}_2^-$  (circles) at 0.5 Torr and the reaction  $\text{SF}_3^+ + \text{SF}_5^-$  (triangles) at 0.7 Torr at room temperature. The binary ion-ion recombination coefficients are deduced from the slopes of the linear portions of the curves and the upcurving of the  $\text{NO}^+ + \text{NO}_2^-$  data at late afterglow times is a manifestation of the increasing importance of diffusion losses at the lower ion densities. The time scale has an arbitrary zero. Note the higher initial density in the  $\text{SF}_3^+ + \text{SF}_5^-$  study due to rapid electron attachment in  $\text{SF}_6$ .

is especially valuable in the determination of the mean ionic mass when more than one species of positive or negative ion is present in the plasma (Smith et al, 1978), and also can act as a confirmation that the ion content of the plasma as determined by the downstream mass spectrometer also applies to the upstream recombination controlled reaction region.

The value of  $\alpha_2$  for reaction (20), i.e.  $\alpha_2(20)$ , at 300 K was measured to be  $(6.4 \pm 0.7) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  (Smith and Church, 1976). The uncertainty in  $\alpha_2$  is largely due to the uncertainty in the probe area ( $\sim 10\%$ ) and to smaller errors in  $v_p$  and in the best fit slope to the reciprocal density plots. The first measurement of  $\alpha_2$  was perplexing in that it was very much smaller than both the value of  $(51 \pm 15) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  deduced from merged beam data (Peterson et al, 1971) and the value of  $(17.5 \pm 6) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  obtained from stationary afterglow data (Eisner and Hirsh, 1971) yet within a factor of two of the absorbing sphere theoretical upper-limit estimate of  $(12 \pm 3) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  (Olson 1972). Clearly further work was necessary to resolve such serious discrepancies.

The reaction:



was also studied in the FALP (Smith and Church, 1976). The conversion of  $\text{NO}_2^-$  to  $\text{NO}_3^-$  in the afterglow was achieved simply by increasing the  $\text{NO}_2$  partial pressure to about 10 mTorr which promoted the reaction of  $\text{NO}_2^-$  with the  $\text{HNO}_3$  impurity in the  $\text{NO}_2$  (Fehsenfeld et al, 1975):



without changing the identity of the positive ion,  $\text{NO}^+$  (further increase in the  $\text{NO}_2$  partial pressure resulted in the production of cluster ions, see below). Thus  $\alpha_2(24)$  was determined under very similar conditions (pressure, flow velocity etc.) to  $\alpha_2(20)$  and was found to be  $(5.7 \pm 0.8) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  at 300 K, again much smaller than the merged beam value  $(81 \pm 23) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ , (Aberth et al, 1971) and within a factor of two of the absorbing sphere theoretical estimate  $((11 \pm 3) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1})$ . It is however somewhat larger than the stationary afterglow value  $((3.4 \pm 1.2) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1})$ .

What are the causes of these large discrepancies? Little comment can be made on the stationary afterglow results since a detailed critique of them has not been published. However it can be said that since these measurements were carried out at pressures of  $\geq 10$  Torr then a three-body contribution to  $\alpha_2$  is to be expected and such was not accounted for. Our preliminary data

TABLE 1

Compilation of the binary ion-ion recombination coefficients,  $\alpha_2$ , for simple molecular ions as determined in the FALP apparatus at room temperature. Also included are the average cross-sections,  $\bar{\sigma}_2$ , calculated by dividing  $\alpha_2$  by the mean relative velocity  $\bar{v}_r (= (8kT/\pi\mu)^{1/2})$  of the reactant ions. In cases where there is more than one reactant positive ion their percentage concentrations are given in parentheses.

Positive Ions	Negative Ions	$\alpha_2 \times 10^8 \text{ cm}^3 \text{ s}^{-1}$	$\bar{\sigma}_2 \times 10^{12} \text{ cm}^2$	References
$\text{NO}^+$	$\text{NO}_2^-$	6.4	1.1	Smith and Church (1976)
$\text{NO}^+$	$\text{NO}_3^-$	5.7	1.0	
$\text{CCl}_3^+(80), \text{CCl}_2^+(20)$	$\text{Cl}^-$	4.5	0.9	
$\text{CClF}_2^+(90), \text{CCl}_2\text{F}^+(10)$	$\text{Cl}^-$	4.1	0.8	
$\text{SF}_3^+$	$\text{SF}_5^-$	4.0	1.2	Church and Smith (1977)
$\text{SF}_5^+$	$\text{SF}_6^-$	3.9	1.3	
$\text{NH}_4^+$	$\text{Cl}^-$	6.7	0.9	Smith et al (1978)
$\text{NO}^+(70), \text{NH}_4^+(30)$	$\text{NO}_2^-$	6.3	1.0	
$\text{Cl}_2^+$	$\text{Cl}^-$	5.0	1.0	Church and Smith (1978)
$\text{O}_2^+$	$\text{CO}_3^-$	9.5	1.7	
$\text{CF}_3^+$	$\text{F}^-$	5.8	0.9	Unpublished data
$\text{NF}_2^+$	$\text{F}^-$	7.5	1.1	
$\text{N}_2\text{F}^+$	$\text{F}^-$	8.5	1.2	

on collision-enhanced recombination which is referred to later (reaction (33), Section 7) shows that at about 10 Torr in helium, the effective binary recombination coefficient is about a factor of two above the low pressure value,  $\alpha_2(20)$ , and that it could be even greater for a nitrogen third body (as was used in the stationary afterglow experiments). Thus the large stationary afterglow value for  $\alpha_2(20)$  can be accounted for, but the low value for  $\alpha_2(24)$  is difficult to understand (indeed it would be further reduced by accounting for the collision-enhanced contribution). We can only tentatively suggest that not all of the  $\text{NO}_3^-$  production processes had been accounted for in the analysis and that perhaps a further reaction such as reaction (25) was also occurring in the afterglow.

The discrepancy between the FALP and merged beam data almost certainly lies in the differing nature of the techniques. Whilst the flowing afterglow is a collision dominated medium in which the internal states of the reactant ions are most probably thermalised, this may not be the case for the ions in the merged beams. Moseley et al (1975) have discussed the possibility of excitation in the  $\text{NO}^+$ ,  $\text{NO}_2^+$  and  $\text{NO}_3^+$  ions and also have shown by experiment that no appreciable fraction of the  $\text{NO}^+$  is excited to the metastable state ( $a^3\Sigma$ ). They concluded that a possible reason for their surprisingly large values of  $\alpha_2(20)$  and  $\alpha_2(24)$  may be the presence of internal excitation of the  $\text{NO}_2^+$  and  $\text{NO}_3^+$  which, in effect, lowers the electron affinities of the  $\text{NO}_2^-$  and  $\text{NO}_3^-$  or, equivalently, reduces the electron detachment energy,  $D_E$ , of the negative ions (for example  $\text{NO}_3^-$  may be in the peroxy form viz.  $\text{O}^-\text{.NO}_2$ ). According to theory (Olson, 1972; Hickman, 1979) this would lead to an enhancement of  $\alpha_2$  for these reactions. Unfortunately there are no other reactions which have been studied in both the FALP and the merged beam experiments from which to search for further insight into the reasons for these discrepancies.

$\alpha_2$  for several other reactions involving simple molecular ions have been determined with the FALP and these are listed in Table 1. Note the small variation in  $\alpha_2$ . Note also that data have been obtained from plasmas in which no single positive ion is dominant. In such cases an average  $\alpha_2$  can be obtained provided that the  $n_-$  vs time plots are linear,  $n_-$  being calculated using  $m_-$ , the mass of the single negative ion species. The mean positive ion mass can be obtained from the ion mass ratio measured by the probe and compared with that obtained from the mass spectrometer data.

It is in the nature of the present FALP technique that it is only practicable to study reactions involving negative ions with relatively large values of  $D_E$  such as those in Table 1. The absorbing sphere theory predicts that  $\alpha_2$  will be largest for reactions involving negative ions with small  $D_E$ , and Hickman (1979)

has shown from such theoretical considerations that  $\alpha_2$  is expected to vary as  $\mu^{-1/2} D_E^{-1/2}$ , where  $\mu$  is the reduced mass of the ion pair. From a consideration of the merged beam and FALP data he has suggested that the best fit to the data is when  $\lambda \approx -0.4$  although when all of the experimental data are considered, a dependence of  $\alpha_2$  on  $D_E$  is not obvious. It remains an important objective to develop the FALP technique in order to study reactions of ions with small  $D_E$ .

The small spread in  $\alpha_2$  for the reactions listed in Table 1 is expected from the absorbing sphere model because of the multiplicity of possible product states in all of these reactions. Thus  $\alpha_2$  at 300 K is seen to lie within the narrow range  $(4 - 10) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  for these simple molecular ion reactions and also, somewhat surprisingly, for the cluster ion reactions discussed in Section 4 (see also Table 2). Also included in Table 1 are the equivalent mean thermal cross-sections  $\overline{\sigma}_2 (= \alpha_2 / \sqrt{v})$  for the reactions for direct comparison with beam measurements. Note the very large values of  $\overline{\sigma}_2$  ( $\sim 10^{-12} \text{ cm}^2$ ). Note also that the few reactions which have been studied which evolve only atomic ions have much smaller  $\alpha_2$  values consistent with the availability of fewer product states (Section 5).

### 3.2 Temperature Dependence Studies

Only a limited amount of FALP data have been obtained to date on the temperature dependence of  $\alpha_2$  (Smith and Church, 1977). These relate to only two reactions i.e. reaction (20) and also the reaction:



Data below room temperature were obtained by surrounding the flow tube with solid carbon dioxide and above room temperature by surrounding the flow tube with an oven. The maximum temperature range covered was 180 K to 530 K. During the low temperature measurements great care had to be taken to ensure that as little of the reactant gases as possible were used to prevent appreciable clustering of the positive and negative ions. This was especially the case when studying reaction (26) since  $\text{NH}_4^+ \cdot (\text{NH}_3)_n$  clusters can form rapidly at low temperatures. The data obtained for reactions (20) and (26) can be described by a simple power law relationship of the form  $\alpha_2 \sim A_1 T^{-n}$  or alternatively as  $\overline{\sigma}_2 \sim A_2 T^{-(n+0.5)}$ . For reaction (20):

$$\alpha_2 = 6.8 T^{-0.4} \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \quad (27)$$

$$\overline{\sigma}_2 = 2.0 T^{-0.9} \times 10^{-10} \text{ cm}^2 \quad (28)$$



The absorbing sphere model (Olson, 1972) predicts that  $\alpha_2 \sim T^{-1}$  and  $\overline{\sigma}_2 \sim T^{-1}$  in the low temperature regime. Thus the FALP data for reaction (20) are quite consistent with these predictions. Also the data for reaction (26), whilst being more limited, are not inconsistent with the theoretical predictions.

The satisfactory agreement between the FALP data and theory, both in the magnitude and the temperature dependence of  $\alpha_2$ , lends credence to both theory and experiment. Since for many reactions  $\alpha_2$  can be determined at 300 K but not at lower temperatures it is extremely useful to be able to assume that  $\alpha_2$  varies as  $T^{-2}$  and thus to obtain estimates of  $\alpha_2$  at low temperatures. We have adopted the  $T^{-2}$  dependence to estimate appropriate values of  $\alpha_2$  for both simple and cluster ion reactions which occur in the Earth's atmosphere (Smith and Church, 1977). A variable-temperature FALP recently constructed in our laboratories which can operate readily over a temperature range of 80 K to 600 K will be used to provide further information on the variation of  $\alpha_2$  with temperature for other reactions.

#### 4. DETERMINATION OF BINARY IONIC RECOMBINATION COEFFICIENTS: CLUSTER IONS

Cluster ions are important components of ionized gases at pressures sufficiently high to promote ternary association reactions and especially important when polar molecules are present. Cluster positive and negative ions are the only ion types present in the lower atmosphere and this was a prime motivation for determining the ionic recombination coefficients for cluster ion reactions in the FALP apparatus. Additional motivation followed from the suggestion by F.T. Smith and his co-workers (Smith et al, 1973; Bennett et al, 1974) that recombination of cluster ions containing an appreciable number of clustered molecules,  $n$ , could be much more efficient than that of the simple 'core' ions alone. Bennett et al (1974) have pointed out that if  $n$  is large enough then the clustered ions would be more stable than the product neutrals and consequently that recombination via electron transitions near crossings of potential curves could not occur. Instead contact or hard-impact collisions would occur followed by coalescence of the ion pair and 'boiling-off' of neutral molecules. Based on this model, an expression was derived for the lower limit to  $\alpha_2$  which contained a parameter  $R_C$ , the sum of the effective radii of the ions, analogous to the radius of the absorbing sphere,  $R_p$ , in Olson's model. We will discuss this model briefly in relation to the FALP data below. F.T. Smith et al (1973) also introduced the concept of 'tidal trapping' of the ions in which they envisaged the excitation of internal modes of vibration and rotation of the ions as they orbit each other in the Coulombic field. Thus kinetic energy of motion is converted into internal energy and the ions can become bound this

TABLE 2

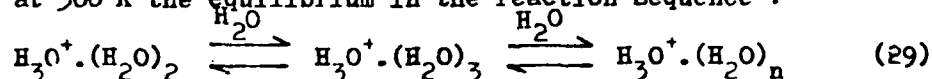
Compilation of binary ion-ion recombination coefficients,  $\alpha_2$ , for cluster ions as determined in the FALP apparatus at room temperature. For other information concerning nomenclature refer to the caption to Table 1. The range of  $\bar{\sigma}_2$  values for reactions involving more than one ionic species of either sign is a reflection of the different masses of these ions.

Positive Ions	Negative Ions	$\alpha_2 \times 10^8 \text{ cm}^3 \text{ s}^{-1}$	$\bar{\sigma}_2 \times 10^{12} \text{ cm}^2$	Reference	
$\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$	$\text{NO}_3^-$	5.5	1.3	Smith et al (1976)	
$\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$	$\text{NO}_3^-\text{HNO}_3$	5.7	1.5		
$\text{NO}^+(\text{NO}_2)_2$	$\text{NO}_3^-(\text{HNO}_3)_3$	4.5*	2.1*	Smith and Chance (1977)	
$\text{NH}_4^+(\text{NH}_3)_2$	$\text{Cl}^-$	7.9	1.4		
$\text{NH}_4^+(\text{NH}_3)_2$	$\text{NO}_2^-$	4.9	0.9	Smith et al (1978)	
$\text{NH}_4^+(\text{NH}_3)_2$ (67)	$\text{NO}_2^-$	5.5	1.1-1.3		
$\text{NH}_4^+(\text{NH}_3)_3$ (53)					
$\text{NH}_4^+(31), \text{NO}^+(25)$					
$\text{NH}_4^+\text{NH}_3$ (25)	$\text{NO}_2^-(47), \text{NO}_3^-(55)$	9.6	1.3-2.0		
$\text{NH}_4^+(\text{NH}_3)_2$ (19)					
$\text{NH}_4^+(16), \text{NO}^+(16), \text{NO}_2^+(19)$	$\text{NO}_3^-(19)$	5.8	0.9-1.5		
$\text{NH}_4^+\text{NH}_3$ (23)	$\text{NO}_3^-\text{HNO}_3$ (38)				
$\text{NH}_4^+(\text{NH}_3)_2$ (26)	$\text{NO}_3^-(\text{HNO}_3)_2$ (43)				
$\text{NH}_4^+\text{NH}_3$ (27)	$\text{NO}_3^-(30)$	6.1	1.2-1.7		
$\text{NH}_4^+(\text{NH}_3)_2$ (33)	$\text{NO}_3^-\text{HNO}_3$ (33)				
$\text{NH}_4^+(\text{NH}_3)_3$ (40)	$\text{NO}_3^-(\text{HNO}_3)_2$ (37)				
$\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$	$\text{HSO}_4^-(30), \text{NO}_3^-\text{H}_2\text{O}$ (30)	5.9	1.4-1.6	Smith et al (1981)	
	$\text{NO}_3^-\text{HNO}_3$ (15) > 140 mm (25)				
$\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$	$\text{HSO}_4^-(35), \text{HSO}_3^-\text{H}_2\text{O}$ (25)	6.6	1.6-1.7		
	$\text{HSO}_2^-\text{H}_2\text{O}$ (20), $\text{NO}_3^-(20)$				
$\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$	$\text{Cl}^-$ (> 95)	6.8	1.3		
$\text{H}^+(\text{H}_2\text{O}) \cdot (\text{CH}_3\text{CN})_3$	$\text{NO}_3^-(65), \text{NO}_2^-(35)$	6.3	1.5-1.7		
$\text{H}^+(\text{H}_2\text{O}) \cdot (\text{CH}_3\text{CN})_3$	$\text{NO}_3^-\text{HNO}_3$ (60), $\text{NO}_3^-(40)$	5.9	1.5-1.9		
$\text{H}^+(\text{H}_2\text{O}) \cdot (\text{CH}_3\text{CN})_3$	$\text{NO}_3^-\text{HNO}_3$ (40), $\text{HSO}_4^-(30)$	5.9	1.8-2.0		
	> 140 mm (30)				
$\text{H}^+(\text{H}_2\text{O}) \cdot (\text{CH}_3\text{CN})_3$	$\text{HSO}_4^-(30), \text{NO}_3^-(30)$	5.8	1.7-1.8		
	$\text{HSO}_2^-\text{H}_2\text{O}$ (25)				
	$\text{HSO}_3^-\text{H}_2\text{O}$ (15)				
$\text{NO}^+(\text{NO}_2)_2$	$\text{NO}_3^-\text{NO}_2$ (40), $\text{NO}_3^-\text{NO}_2$ (35)	6.5	1.2-1.3		
	> 140 mm (25)				

\* the  $\alpha_2$  and  $\bar{\sigma}_2$  values quoted are the values at 182 K. When calculated for a temperature of 300 K, assuming that  $\alpha_2 \sim T^{-1}$  and  $\bar{\sigma}_2 \sim T^{-1}$  (See section 3.2), they become  $3.5 \pm 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  and  $1.2 \pm 10^{-12} \text{ cm}^2$  respectively.

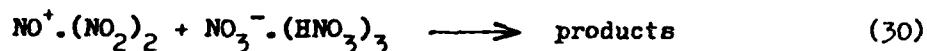
ultimately resulting in recombination. This process can take place irrespective of whether or not the ion pair is more stable than the neutrals, but the magnitude of  $\alpha_2$  depends on the probability that trapping occurs which in turn depends in an uncertain way on  $n$  but is expected to be appreciable only for  $n \gtrsim 6$ . An upper limit to  $\alpha_2$  has been formulated from this model for water cluster ions as  $5 \times 10^{-7} (300/T) (6/n)^2 \text{ cm}^3 \text{ s}^{-1}$ .

The experimental determination of  $\alpha_2$  for cluster ion reactions is more challenging experimentally since it is difficult to create ion-ion plasmas of sufficient ionization density containing a single species of either cluster positive or negative ions. However this has been achieved in several cases; notably ion-ion plasmas have been created containing  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$  as the only positive ion species as well as plasmas containing only the ammonia cluster ions  $\text{NH}_4^+(\text{NH}_3)_{1,2,3}$ , together with single negative ion species both simple and clustered (Smith et al, 1976, 1978). It is fortunate that the  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$  ion is a stable terminating positive ion under flowing afterglow conditions at 300 K and that even in the presence of large concentrations of water vapour the next highest order cluster  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_4$  does not exist in significant concentrations. Thus at 300 K the equilibrium in the reaction sequence :



is overwhelmingly in favour of the  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ . Similarly plasmas can be created which favour the production of the  $\text{NH}_4^+(\text{NH}_3)_2$  ion. Chlorine is an especially useful gas in these studies since it rapidly produces  $\text{Cl}^-$  ions yet it is not very prone to cluster to ions. Similarly  $\text{NO}_2$  is a valuable source of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  ions. Thus it has been possible to determine  $\alpha_2$  for the reactions of several cluster positive ion species with these simple negative ion species and these data are included in Table 2 together with our other data on cluster ion reactions, including some reactions in which both the positive and negative ion species are clustered. For those plasmas in which more than one species of positive and/or negative ion clusters co-exist, the Langmuir probe determination of the mean mass ratio  $m_+/m_-$  is a vital addition to the mass spectrometry data, since it can indicate where any change in the ion types occurs along the afterglow plasma column. Only those systems were studied seriously for which there was no such change in the ion types and for which reciprocal density plots were linear over at least about a factor of 4. Under conditions for which more than one ionic species of either charge were present then an average  $\alpha_2$  was obtained. The most recent data included in Table 2 relates to the reactions of some positive and negative ions which have recently been detected in the stratosphere, specifically the reactions of  $\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{CN})_3$  ions (Smith et al, 1981).

A glance at the  $\alpha_2$  values given in Table 2 shows that they are not significantly different than those for the simple molecular ion reactions (Table 1). In view of the theoretical postulates referred to above these were somewhat surprising results. The reaction involving the most heavily-clustered ions :



which was studied at 182 K in order to enhance the degree of clustering, has the smallest  $\alpha_2$  but the largest  $\bar{\sigma}_2$  (a consequence of the large reduced mass and the lower temperature). When  $\bar{\sigma}_2$  for this reaction is calculated for a temperature of 300 K (assuming  $\bar{\sigma}_2 \sim T^{-1}$ ), for comparison with the other data, then it is not appreciably larger than the  $\bar{\sigma}_2$  for the other cluster ion reactions. For the reactions of these moderately-sized cluster ions there is no indication of significant enhancement of  $\alpha_2$  above those for the simple molecular ions, and the  $\bar{\sigma}_2$  are only just a little larger on average. Therefore as expected, tidal trapping is not occurring to an appreciable extent in these cluster ion reactions.

It remains to ask to what extent contact collisions followed by coalescence are involved in these reactions. Bates (1979) has considered this problem and has calculated values for  $R_T$  (the effective absorbing radii for the interactions referred to above) using the experimentally determined  $\alpha_2$  for several of the reactions given in Table 2. He showed that the values obtained (typically 8Å) are greater than would be expected for  $R_C$  (~ 4Å) but within the range of  $R_T$  that Olson (1972) calculated for simple ion reactions. It seems probable therefore that ionic recombination via electron transitions near curve crossings occurs in most of the reactions studied, although for those reactions involving the largest cluster ions (such as reaction (30)) then this may be energetically unfavourable (as mentioned above) since the ion pair can become more stable than their neutral counterparts. This results when the recombination energy of the positive ion (which is effectively reduced by the presence of cluster molecules) becomes less than the electron detachment energy of the negative ion (which is effectively increased by the presence of cluster molecules). Under these circumstances coalescence of the ion pair can occur within which the charges remain separated forming a kind of "zwitterion".

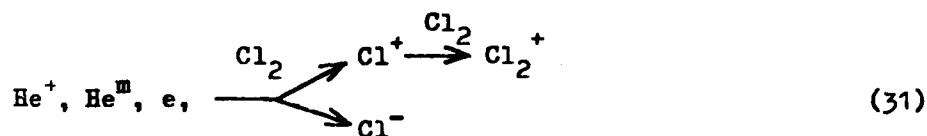
What are now needed are data relating to reactions at much larger cluster ions (i.e. for  $n > 6$ ) for which the tidal trapping model predicts significantly larger recombination coefficients. This would assist theorists in this most difficult area. However the experimental difficulties involved in such measurements are great, although further experiments at lower temperatures in our laboratory offer some hope of determining  $\alpha_2$  for larger clusters. Unfortunately, it seems unlikely that we will be able to directly

obtain the variation of  $\alpha_2$  with temperature for a given cluster ion reaction because the rapid change with temperature of ternary ion-molecule association reactions results in changes in the degree of clustering to both positive and negative ions.

## 5. IONIC RECOMBINATION REACTIONS: ATOMIC IONS

The large rate coefficients for the ionic recombination reactions involving both simple and cluster ions are largely due to the large number of possible product channels in these reactions. However, when both the positive and negative ions are atomic then from such considerations the  $\alpha_2$  may be much smaller since there are many fewer possible product states. For such systems detailed curve crossing calculations may be made. Olson (1977) has calculated the  $\alpha_2$  and their temperature dependencies for the reactions  $\text{Na}^+ + \text{Cl}^-$  and  $\text{K}^+ + \text{Cl}^-$ . The values at 300 K are  $9.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and  $1.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  respectively, more than two orders-of-magnitude smaller than those typical of molecular ion recombination reactions. Experimental support for Olson's calculations has been obtained by Burdett and Hayhurst (1977) from their flame plasma studies. More data on atomic ion systems are required so that more such comparisons can be made with theory.

Determination of  $\alpha_2$  for atomic ion reactions in the FALP necessarily requires the generation of afterglow plasmas comprised of sufficiently high densities of atomic ions only, an interesting challenge in itself. The addition to an helium afterglow of any gas which generates stable negative ions also generates molecular positive ions. For example,  $\text{Cl}_2$  addition to the helium afterglow initiates the following reaction sequence :



Thus, the  $\text{Cl}^-$  ion forms via thermal dissociative attachment (Section 2.1.3) but unfortunately  $\text{Cl}_2^+$  ions are formed also. This problem has been avoided however by the following procedure (see Church and Smith, 1978). The usual microwave cavity discharge was used to generate the primary ionization and a short distance downstream the afterglow plasma was exposed to a second microwave cavity in which the field was insufficiently intense to discharge the gas but intense enough to heat the plasma electrons to greatly enhance the ambipolar diffusive loss of both electrons and positive ions. Thus all of the electrons and positive ions were excluded from the carrier gas and only helium metastable atoms,  $\text{He}^{\text{m}}$  (mainly  $2^3\text{S}$  with some  $2^1\text{S}$ ), remained to be convected down the flow tube (Smith et al, 1975). A rare gas (Ar, Kr or Xe) was then added in a sufficient quantity

to destroy all of the  $\text{He}^m$  thus generating the rare gas atomic ions ( $\text{Ar}^+$ ,  $\text{Kr}^+$  or  $\text{Xe}^+$ ) and electrons but insufficient to result in the conversion of the atomic rare gas ions to molecular rare gas ions (Smith et al, 1972b). A suitable halogen gas ( $\text{F}_2$  or  $\text{Cl}_2$ ) was then added further downstream which generated the negative ions ( $\text{F}^-$  or  $\text{Cl}^-$ ) via thermal dissociative attachment but which could not be ionized by the rare gas positive ions. By this technique  $\text{Ar}^+ + \text{F}^-$ ,  $\text{Kr}^+ + \text{F}^-$ ,  $\text{Xe}^+ + \text{F}^-$  and  $\text{Xe}^+ + \text{Cl}^-$  afterglow plasmas were generated and the decay of ionization in them studied.  $\text{Kr}^+ + \text{Cl}^-$  and  $\text{Ar}^+ + \text{Cl}^-$  plasmas could not be created since both  $\text{Kr}^+$  and  $\text{Ar}^+$  charge transfer with  $\text{Cl}_2$  producing unwanted  $\text{Cl}_2^+$  ions.

It was immediately apparent that the  $\alpha_2$  for all of the reactions studied were much smaller than those for molecular ion reactions because the gradients of ionization density along the afterglow columns were very much smaller than in the molecular ion plasmas. In fact the axial gradient of ionization density was closely exponential (see Church and Smith, 1978) indicating that the only significant loss process for the ions was ambipolar diffusion. Values of the ambipolar diffusion coefficients  $D_{+,-}$  were obtained which are in good agreement with those calculated from mobility data. Thus only upper limits to  $\alpha_2$  could be obtained these being  $\sim 5 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$  for the  $\text{Xe}^+ + \text{Cl}^-$ ,  $\text{Xe}^+ + \text{F}^-$  and  $\text{Kr}^+ + \text{F}^-$  reactions and  $\sim 1 \times 10^{-8} \text{cm}^3 \text{s}^{-1}$  for the  $\text{Ar}^+ + \text{F}^-$  reaction.

In order to place a closer limit on  $\alpha_2$  for the  $\text{Ar}^+ + \text{F}^-$  reaction it was further investigated using argon as the carrier gas rather than helium, since diffusion coefficients of ions in argon are much smaller than in helium (see McDaniel and Mason, 1973). Thus a small amount of  $\text{F}_2$  was introduced into a pure argon afterglow (argon pressure  $\sim 0.3$  Torr) whence  $\text{F}^-$  rapidly formed via thermal dissociative attachment. As before the  $\text{Ar}^+$  ions were unaffected since they cannot charge transfer with  $\text{F}_2$ . Again the measurement of the axial ion density gradient indicated only diffusive loss of ions but at a much slower rate than in the helium carrier gas thus allowing a reduced upper limit to be placed on  $\alpha_2$  for the  $\text{Ar}^+ + \text{F}^-$  reaction of  $\sim 2 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$ . Unfortunately the other rare gas positive ion/halide negative ion reactions cannot be studied using an argon carrier gas since  $\text{Ar}^+$  charge transfers with  $\text{Cl}_2$  and the Penning ionization technique is not possible because  $\text{Ar}^m$  atoms cannot ionize Kr or Xe. The use of higher pressures of the argon carrier gas can in principle assist in obtaining closer limits to  $\alpha_2$  for slow reactions, although at much higher pressures in argon the probe technique becomes suspect due to collisions of ions in the space charge sheath which forms around the probe.

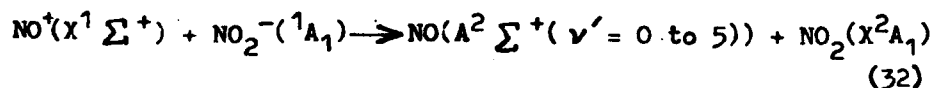
The  $\alpha_2$  for these atomic ions reactions are at least one order-of-magnitude smaller than those typical of molecular ion reactions. Although to our knowledge no calculations of  $\alpha_2$  have been made for these reactions the small values are consistent with expectations

because in these systems very few possible product channels are available. Other atomic ion reactions studied using the merged beam technique (Moseley et al, 1975) have much larger ionic recombination cross-sections (and hence larger  $\alpha_2$  values). So whilst the  $\alpha_2$  values for reactions involving molecular ions do not show great variations, those for atomic ions clearly vary widely and each reaction needs individual consideration.

## 6. PRODUCTS OF BINARY IONIC RECOMBINATION REACTIONS

In addition to the determination of  $\alpha_2$  for ionic recombination reactions it is clearly desirable to determine the nature of the neutral products and the energy partition in the reactions. This very difficult problem has received little attention from experimentalists and to our knowledge only two reactions have been studied. Weiner et al (1970, 1971), using a merged beam apparatus, have studied as a function of interaction energy the optical emissions from the atomic energy levels in the Na atoms which are populated following the neutralization reaction  $\text{Na}^+ + \text{O}^-$  and deduced reaction cross-sections for the population of individual atomic levels. Moseley et al (1972) have measured the total cross-section for this reaction as a function of energy and obtained values irreconcilably lower than those of Weiner et al for the single  $\text{Na}(3^2\text{P})$  product. The determination of absolute cross-sections from optical emission studies is difficult and the inconsistency may be due to calibration errors in these experiments. However this cannot detract from the considerable importance of this pioneering work. Further useful work on atomic ion systems is clearly possible with this kind of technique and would be of great value.

Optical emission studies of molecular ion recombination reactions are expected to be considerably more complicated than for the atomic ion reactions but a start has been made in a study of the emission from a  $\text{NO}^+/\text{NO}_2^-$  thermalized afterglow (Smith et al, 1978) in an attempt to identify the products of reaction (20). The emission spectrum of the afterglow plasma was investigated in the wavelength range 180 - 600 nm and the only significant radiations identified were the  $\gamma$ -bands of NO. Proof that this radiation was being emitted from the NO formed in the reaction was obtained from the close correlation between the emitted intensity in the  $\gamma$ -bands and the square of the ion density in the afterglow volume from which the radiation was emitted, as is expected for a recombination controlled plasma (see equation (17)). Therefore it was argued that the reaction proceeded thus :



Some population of NO ( $C^2\Pi$ ) and NO ( $D^2\Sigma^+$ ) or some vibrational excitation of the NO<sub>2</sub> ( $X^2A_1$ ) could not be ruled out entirely (although from energy considerations both cannot occur in a single interaction). A discussion of the details of the measurements is given by Smith et al (1978). Inspection of the potential curves shows that an electron transfer from the NO<sub>2</sub><sup>-</sup> into the lowest vibrational state of NO ( $A^2\Sigma^+$ ) will occur at an internuclear separation of about 1 nm and therefore that the product molecules will possess a net kinetic energy of about 1.4 eV. If the product NO and/or NO<sub>2</sub> are vibrationally excited then, of course, the net kinetic energy in the products will be correspondingly smaller. Sufficiently high resolution spectroscopy could perhaps detect the Doppler broadening on the rotational structure of the NO  $\gamma$ -bands.

This is just the beginning of what could be a very profitable approach to the study of the products of ionic recombination reactions. Further work along these lines is planned for simple ion reactions. Laser resonance fluorescence studies on the product neutrals should also be a viable proposition in flowing afterglow plasmas considering the relatively high density of product neutrals involved ( $\sim 10^{10}\text{cm}^{-3}$ ).

## 7. PRELIMINARY STUDIES OF COLLISION-ENHANCED IONIC RECOMBINATION

It was mentioned in Section 1 that the ternary ionic recombination process (2) was studied extensively during the first half of this century, most effort then being directed towards the so-called Thomson regime (the intermediate pressure region  $\sim 100 - 1000$  Torr) and the so-called Langevin-Harper regime (the high pressure region above about 1000 Torr). More recent work has extended the investigations to pressures as low as a few tens of Torr (Mahan and Person, 1964; McGowan, 1967; Sennhauser and Armstrong, 1978a,b). There is a need to study ionic recombination at the lower pressures at which the pure binary process just begins to be enhanced by collisional effects. Such a situation obtains in the middle stratosphere, a regime currently being probed using balloon-borne instruments and in which ionic recombination rate data are required for de-ionization rate calculations (Arnold, 1980). Previous estimates of "effective binary recombination coefficients" in the low pressure regime were obtained by the doubtful procedure of extrapolating higher pressure data.

In order to provide data in this low pressure regime we have studied the collision-enhanced ionic recombination coefficient,  $\alpha_2$ , for two reactions up to a pressure of 8 Torr in helium (the maximum available with the present FALP technique, Smith and Adams, 1980b).



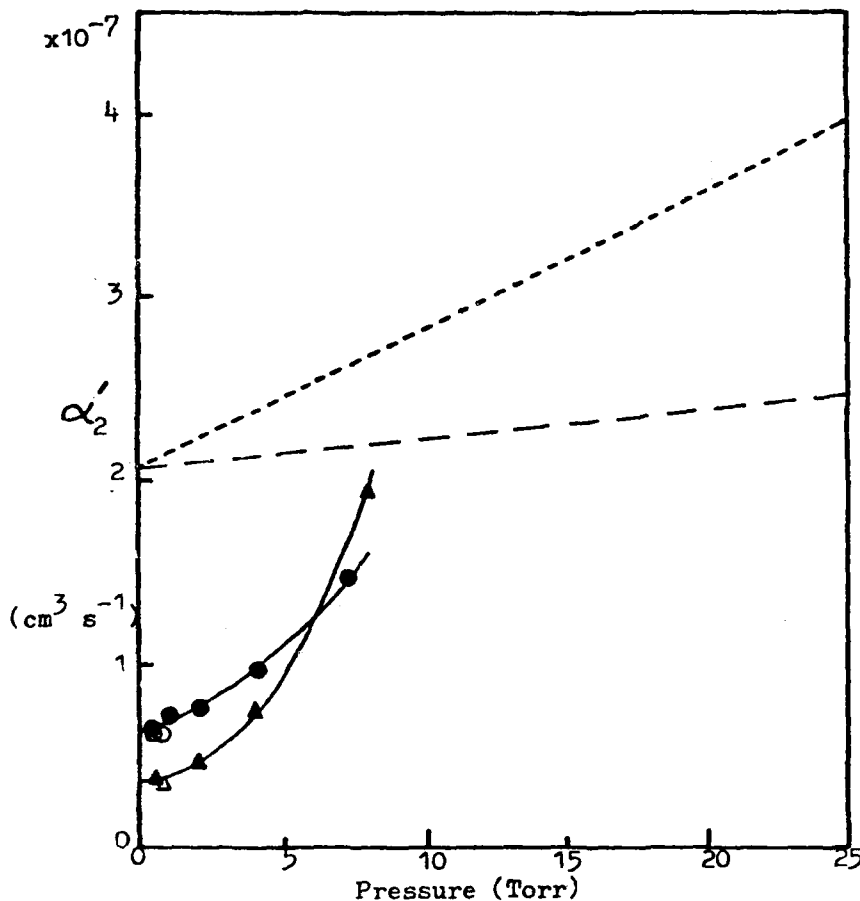
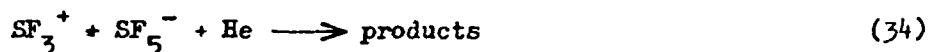


Fig.3 Collision-enhanced ionic recombination coefficients,  $\alpha_2'$ , as a function of pressure at room temperature for the reactions  $\text{NO}^+ + \text{NO}_2^- + \text{He}$  (filled circles) and  $\text{SF}_3^+ + \text{SF}_5^- + \text{He}$  (filled triangles). Also included are the binary ionic recombination coefficients,  $\alpha_2$ , of Smith and Church (1976) for the  $\text{NO}^+ + \text{NO}_2^-$  reaction (open circles) and Church and Smith (1977) for the  $\text{SF}_3^+ + \text{SF}_5^-$  reaction (open triangle). The dashed lines represent a linear extrapolation to lower pressures of the data of Mahan and Person (1964) ostensibly for the reactions  $\text{NO}^+ + \text{NO}_2^- + \text{He}$  (long dashes) and  $\text{NO}^+ + \text{NO}_2^- + \text{N}_2$  (short dashes); see Section 7.

They are :



The ions were generated in the flowing afterglow in the usual way and the  $\alpha_2$  were obtained at several pressures from the slopes of the reciprocal density plots as described previously. The results obtained are presented graphically in Fig. 3 as plots of  $\alpha_2$  against helium pressure where it is apparent that  $\alpha_2$  is sensibly independent of pressure below about 1 Torr. Note the good agreement between the present and previously published values for  $\alpha_2$ , corroborating the previous result that  $\alpha_2(33)$  is significantly larger than  $\alpha_2(34)$ . The increase in  $\alpha_2(34)$  is about a factor of 5 over the pressure range whereas  $\alpha_2(33)$  only increases by about a factor of 2 and neither increases linearly with pressure. Also included in Fig. 3 is a linear extrapolation of the data of Mahan and Person (1964) ostensibly for reaction (33) from their lower limit of pressure of about 50 Torr. Clearly this extrapolation of their data to pressures below 8 Torr would indicate very different values of  $\alpha_2(33)$  than those obtained in the FALP experiment. This forcibly illustrates that extrapolation of high pressure data to the limit of zero pressure to obtain  $\alpha_2$  is unacceptable (Mahan and Person obtained a value for  $\alpha_2(20)$  of  $2.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  compared to the low pressure FALP value of  $6.4 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  Table 1). Also included in Fig. 3 is an extrapolation of the Mahan and Person data ostensibly for the reaction :



and this clearly demonstrates that  $\text{N}_2$  is a more effective third body catalyst for the recombination reaction ( $\text{N}_2$  is also found to be more effective than He as a stabilizing third body in ion-molecule association reactions - see the review by Good, 1975). It must be stated again however that no mass analysis was performed in the Mahan and Person experiments and so the ions may not be the simple ions  $\text{NO}^+$  and  $\text{NO}_2^-$  but perhaps clusters (e.g.  $\text{NO}^+ \cdot \text{NO}$ ). There is an obvious need for further study of more ionic recombination reactions in this low pressure regime, and for investigations of the dependence of  $\alpha_2$  on the nature of the third body. Also, theory predicts a much more rapid change of the ternary recombination coefficients with temperature ( $\sim T^{-3}$ , Flannery, 1976) than that for the binary coefficients ( $T^{-2}$ ). It is clearly desirable to study the temperature dependence of  $\alpha_2$  to assist in the understanding of this interesting recombination regime.

## 8. SUMMARY AND CONCLUSIONS

Using the FALP apparatus the first reliable data have been obtained on the pure binary ionic recombination coefficients (or mutual neutralization coefficients),  $\alpha_2$ , for the reactions of mass-identified ground-state reactant ions at thermal energies. Thus values of  $\alpha_2$  have been obtained for several reactions involving simple molecular ions and for several reactions involving cluster ions. The values of  $\alpha_2$  at 300 K for all of these reactions are within the limited range  $(4 - 10) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  and are consistent with theoretical expectations for such reactions. The study of the temperature dependence of  $\alpha_2$  for two reactions has shown that they also vary in accordance with theoretical predictions. Upper limits to  $\alpha_2$  have been obtained for a few reactions involving atomic ions only; the very small values for  $\alpha_2$  for these particular reactions are consistent with expectations although this must not be taken as a generalisation for all atomic ion reactions since others are expected to have larger values of  $\alpha_2$  (this has been demonstrated in merged beam experiments). The neutral products and the energy partition in these reactions have not been seriously studied to date; the products of only one reaction ( $\text{NO}^+ + \text{NO}_2^-$ ) have been studied spectroscopically in the FALP apparatus. A start has also been made in the study of collision enhanced ionic recombination in the FALP. This very versatile apparatus can be exploited much more in the study of ionic and electronic recombination reactions at thermal energies.

## ACKNOWLEDGEMENTS

We are indebted to our co-authors of the papers referenced here for their invaluable contributions to this work. We are also grateful to the Science and Engineering Research Council and to the United States Air Force for their financial support of the FALP research programme.

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APPENDIX 2

IONIC RECOMBINATION IN THE STRATOSPHERE

Geophys.Res.Letts. (submitted)

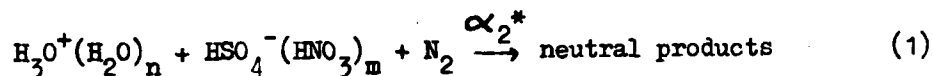
IONIC RECOMBINATION IN THE STRATOSPHERE

D.Smith and N.G.Adams  
Department of Space Research,  
University of Birmingham,  
Birmingham, B15 2TT,  
England.

Abstract. Recent laboratory measurements of positive ion/negative ion recombination coefficients at pressures below 8 torr have indicated that the coefficients increase more rapidly with pressure than expected on the basis of previous higher pressure data. These data, together with previous recombination coefficients obtained in the low pressure limit have been used to redetermine the values for the total effective binary recombination coefficients which are most appropriate to the stratosphere. These new values are almost a factor of two larger than our previous values and are, within error, in agreement with the values derived from in-situ measurements of ion densities and ionization production rates. It is concluded that the new values are accurate to better than  $\pm 50\%$  and can be used with confidence in calculations of stratosphere deionization rates.

### Introduction

Positive ion-negative neutralization (ionic recombination) is the dominant loss mechanism for ionization in the stratosphere. In the lower stratosphere the process of ternary (or three-body) ionic recombination is expected to dominate e.g.

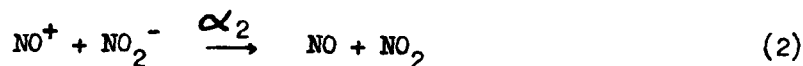


in which the neutralization rate is enhanced at the high ambient gas pressures (i.e. predominantly  $\text{N}_2$ ). An effective binary (or two-body) recombination coefficient  $\alpha_2^*$  can be ascribed to the process and this is, of course, pressure dependent. The first measurements of  $\alpha_2^*$  were carried out several decades ago and clearly showed both its pressure dependence and its magnitude. Subsequent, detailed studies by Mahan and Person (1964, hereafter referred to as the MP data)



vindicated the early data and additionally demonstrated how  $\alpha_2^*$  varied with the nature of the ambient gas (the third body).

At the lower ambient pressures of the upper stratosphere, the process of pure binary mutual neutralization is expected to dominate e.g.



having a pure binary recombination coefficient,  $\alpha_2$ . However, it was only comparatively recently that the pure binary process was studied in any detail. Values of  $\alpha_2$  have been obtained using the flowing after-glow/Langmuir probe (FALP) technique developed in our laboratory and this technique has also been exploited to obtain the new data relevant to this paper. The FALP technique has been described in detail previously (Smith et al, 1975, 1978; Smith and Church, 1976) and  $\alpha_2$  values have been determined for many reactions involving both simple ions (such as those in reaction (2)) and clustered ions (such as those in reaction(1)). References to these data are given in Smith et al, (1981) and in the recent review by Smith and Adams (1982). On the basis of these values of  $\alpha_2$  and the previous values of  $\alpha_2^*$ , Smith and Church (1977) suggested values for the ionic recombination coefficient  $\alpha_T (= \alpha_2 + \alpha_2^*)$  appropriate to the various atmospheric regions.

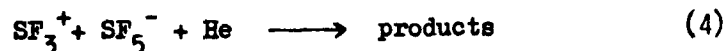
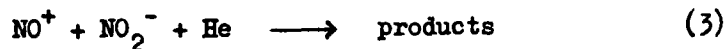
The FALP experiments have indicated that  $\alpha_2$  is not very dependent on the nature or complexity of the ions involved in the reactions ( $\alpha_2$  lies within the limited range  $(4 - 10) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  except where both reactant ions are atomic; see Church and Smith, 1978) and this is also indicated by the MP data for  $\alpha_2^*$ . However, the magnitudes of  $\alpha_2$  are some four times smaller than the values inferred by Mahan and Person from linear extrapolations of their higher pressure data to zero pressure. This

discrepancy initially gave some cause for concern; however this has been dispelled by recent theoretical work which clearly indicates that such linear extrapolations of high pressure data to determine  $\alpha_2$  are entirely unacceptable (Bates and Mendas, 1978). More importantly the quality of both the FALP data and the MP data are such that together they clearly indicate that, in the pressure range from about 1 to 10 torr, ionic recombination must increase more rapidly than would be expected from a consideration of the higher pressure data alone. Again, support for this conclusion is found in recent theoretical work which characterizes the phenomenon of collision enhanced mutual neutralization (Bates and Mendas, 1978; Bates, 1981; Whitten et al, 1982).

Clearly, experimental work is necessary to determine the ionic recombination coefficients in this interesting and stratospherically important pressure regime. Relevant data have now been obtained and on the basis of these data, we have re-estimated the values of  $\alpha_T$  appropriate to stratospheric conditions. Such data have additional significance since they are necessary for calculating the concentrations of the minor neutral constituents of the stratospheric gas from in-situ measurements of ionic concentrations (Arnold et al, 1980, 1981, Viggiano and Arnold, 1981a,b).

#### Laboratory Data

Two reactions have been studied in helium ambient gas over the pressure range 1-8 torr using the FALP technique. They are :



The details of the data have been described in the literature (Smith and Adams, 1982). Unfortunately we were not able to study the reactions in a

nitrogen ambient gas largely due to the extremely 'noisy' nature of the microwave discharge in nitrogen. The important features of the data obtained are as follows. For reaction (3), the total effective binary recombination coefficient,  $\alpha_T (= \alpha_2 + \alpha_2^*)$  increases from low pressure limiting value of  $6.5 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  ( $\equiv \alpha_2$ ) to  $15 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ , and for reaction (4) it increases from  $4 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  ( $\equiv \alpha_2$ ) to  $19 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  over the accessible pressure range. As expected, the rate of increase of  $\alpha_2^*$  with pressure is much more rapid than at higher pressures. The more rapid increase of  $\alpha_2^*$  for reaction (4) is a manifestation of the smaller mobility of the heavier  $\text{SF}_3^+/\text{SF}_5^+$  ions in helium (compared to the  $\text{NO}^+/\text{NO}_2^+$  ions) and hence the closer collisional coupling of the ions with the ambient helium (see Mahan and Person, 1964; Mahan, 1973).

#### Stratospheric Implications

Clearly, for stratospheric calculations, ionic recombination data for the appropriate ion types in nitrogen ambient gas are required. Fortunately, as stated earlier, the nature of the ion types does not markedly influence the recombination coefficient. However the MP studies, which included measurements in both He and  $\text{N}_2$  ambient gases, have forcibly demonstrated the greater efficiency of  $\text{N}_2$  relative to He as a third-body catalyst for ionic recombination. At high pressures,  $\text{N}_2$  is about three to four times more effective than He and we expect that this will also be the case in the lower pressure regime. On this basis we have constructed an  $\alpha_T$  versus  $\text{N}_2$  pressure curve using our  $\alpha_T$  versus He pressure data and have merged this curve with the higher pressure experimental data of Mahan and Person in  $\text{N}_2$ . From this curve we have produced a curve which describes the expected variation of  $\alpha_T$  as a function of altitude

in the stratosphere taking account of the temperature gradients (as defined by the U.S. Standard Atmosphere, 1976), and this curve is shown in Figure 1. The low pressure (mutual neutralization) recombination coefficients,  $\alpha_2$  have been adjusted according to a  $T^{-\frac{1}{2}}$  variation as predicted by theory (Olson, 1972) and as indicated by experiment (Smith et al, 1978), and the high pressure coefficients,  $\alpha_2^*$ , adjusted to the theoretically predicted  $T^{-3}$  variation (Flannery, 1976). Note that this curve differs significantly from that given previously by Smith and Church (1977) only in the 25 to 45 km altitude range (this is solely due to the relatively rapid increase of  $\alpha_2^*$  with pressure revealed by the new laboratory data), and at 35 km the present recombination coefficient is about a factor of two greater than the previous value. In view of the approximations and estimates made, however, these new estimates of  $\alpha_T$  in this altitude range cannot be considered to be accurate to better than  $\pm 50\%$ .

Also included in Figure 1 are the values of  $\alpha_T$  due to Rosen and Hofmann (1981) which they derived from their measurements of positive ion densities and ionization rates in the atmosphere. Considering the possible errors in both approaches the agreement is remarkably good. Interestingly, Rosen and Hofmann suggest that their estimates may be somewhat too small above 32 km in altitude; any small increase in their values of  $\alpha_T$  would clearly bring the two estimates into even closer accord. That the present values for  $\alpha_T$  are greater than those of Rosen and Hofmann between 10 and 20 km may be due in part to the assumed rapid  $T^{-3}$  variation in  $\alpha_2^*$ . It is clear that an experimental investigation of the temperature dependence of  $\alpha_2^*$  is necessary.

### Conclusions

We have made new estimates of the ionic recombination coefficients,  $\alpha_T$ , appropriate to the stratosphere and these are almost a factor of two greater than our previous estimates in the 30 - 40 km altitude range, a region which is currently being investigated using balloon-borne instrumentation. The excellent agreement between the values derived for the recombination coefficients from in-situ ion densities and ionization rates and those based on laboratory data indicates that no major errors are involved in either the laboratory or in-situ measurements or in the assumptions made in deriving the recombination coefficients. Thus, we suggest that our values for  $\alpha_T$  given in Figure 1 can be used with confidence in calculations of stratospheric deionization rates. The values of  $\alpha_T$  in this altitude range are important parameters in the determination of the concentrations of minor neutral constituents from the in-situ measurements in the stratosphere of positive and negative ion densities which are now being obtained.

Acknowledgements. This work was supported by a grant (Grant No. AFOSR-77-3260) from the United States Air Force.

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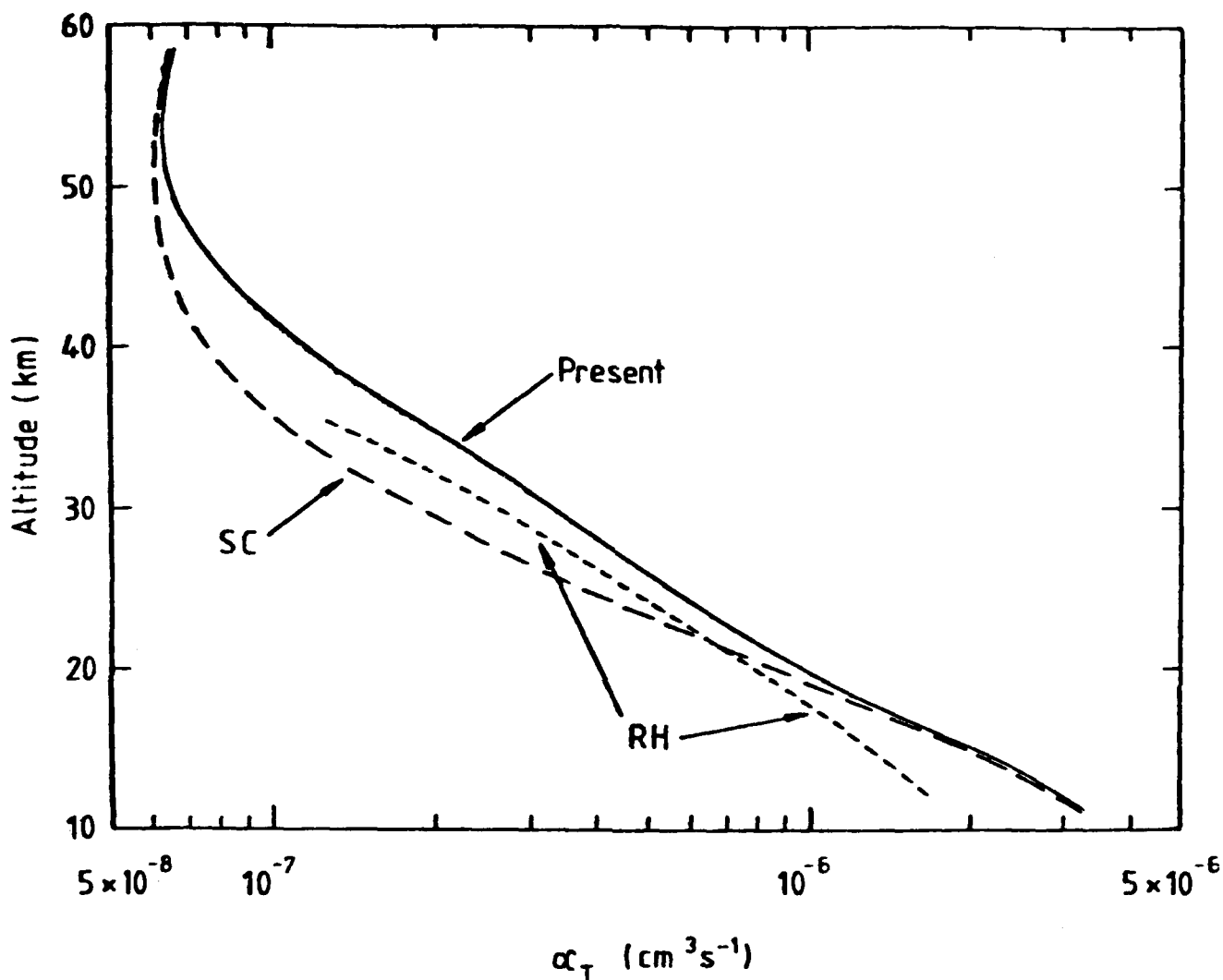


FIG. 1

The total effective binary ionic recombination coefficients,  $\alpha_T$ , in the stratosphere. The solid line represents our estimates which are based on all of the laboratory data now available (see text). SC indicates the earlier estimates of Smith and Church (1977) based on the laboratory data available at that time. RH indicates the estimates of Rosen and Hofmann (1981) derived from in-situ stratospheric measurements of positive ion densities and ionization rates.



**DATE**  
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